Unusual Group 14† Metal Thiolates and Sulphides derived from Tris(trimethylsilyl)methanethiol; *X*-Ray Structures of $[Pb(NR_2)(\mu\text{-}SCR_3)]_2$ and *cis*-$[Ge(CH_2Ph)(NR_2)(\mu\text{-}S)]_2$, (R = $SiMe_3$)‡

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The reaction of tris(trimethylsilyl)methanethiol, $HSCR_3$ (R = $SiMe_3$), with a group 14† metal(II) bis(trimethylsilyl)amide, $M(NR_2)_2$ (M = Ge or Pb), gives unexpected products: *cis*- and *trans*-$[Ge(CH_2Ph)(NR_2)(\mu\text{-}S)]_2$ [a rare example of a group 14 cyclodi(metalthiane), $\{MXX(\mu\text{-}S)\}_2$, by refluxing in PhMe]; $[Pb(SCR_3)(\mu\text{-}SCR_3)]_2$ (the new ligand $\bar{S}CR_3$ evidently can function in both a terminal and a bridging fashion); and $[Pb(NR_2)(\mu\text{-}SCR_3)]_2$, the first simple prochiral group 14 metal(II) complex.

The present results stem from our interest in bulky ligands, especially in the context of the simple bivalent chalcogen-centred ($\bar{O}R'$ and $\bar{S}R'$) compounds of the group 14† elements: the structurally characterised $Sn(SAr)_2$ (Ar = $C_6H_2Bu^t_3$-2,4,6),[1] the lead analogue, $M'(SAr')(\mu\text{-}SAr')_2M'(\mu\text{-}SAr')_2M'(SAr')$ (Ar′ = $C_6H_3Pr^i_2$-2,6, M′ = Sn or Pb), $M''(OCBu^t_3)_2$ (M″ = Ge or Sn),[2] and $[Sn(OBu^t)(\mu\text{-}OBu^t)]_2$. The new ligand $\bar{S}CR_3$ (R = $SiMe_3$), like $\bar{S}Ar$, $\bar{S}Ar'$, $\bar{O}CBu^t_3$, and OBu^t, is bulky and has the potential for conferring lipophilicity on its metal complexes; additionally, however, it has incipiently labile $SiMe_3$ groups and a prospective (*cf.*, ref. 3) free radical chemistry.

Tris(trimethylsilyl)methanethiol was prepared from HCR_3 (R = $SiMe_3$) and successively LiMe, S_8, and acidic hydrolysis[3,4] (we had independently used the same procedure). Its facile C–Si cleavage is evident from its thermal rearrangement into $RSCHR_2$,[3,4] a radical-induced $SiMe_3$ migration which is also promoted by addition of azobisisobutyronitrile or by the photolysis of $HSCR_3$.[3]

Tris(trimethylsilyl)methanethiol was converted, as outlined in Scheme 1, into various metal derivatives: $[Li(SCR_3)]_n$, (**1**), $[M'(SCR_3)_2]_y$ [M′ = Sn, (**2**); or M′ = Pb, *y* = 2, (**3**)], $[Pb(NR_2)(\mu\text{-}SCR_3)]_2$, (**4**), and *cis*- (**5**) and *trans*- (**6**) $[Ge(CH_2Ph)(NR_2)(\mu\text{-}S)]_2$. The new compounds (**1**)—(**6**) have been characterised by elemental analysis and n.m.r. [^1H, ^{13}C, and for (**1**) ^7Li] spectroscopy, and compounds (**4**) and (**5**) by their *X*-ray structures; additionally, poor quality *X*-ray data on compound (**3**) were adequate to establish its structure in the crystal as $[Pb(SCR_3)(\mu\text{-}SCR_3)]_2$.

Features of interest include (i) the potential for a rich co-ordination chemistry of the new ligand $\bar{S}CR_3$; (ii) the prochiral nature of compound (**4**), which is the first simple well characterised stable compound of the group 14 metals of formula $(MXY)_n$ (n = 1 or 2, and X^- and Y^- are monohapto ligands); (iii) the identification of compounds (**5**) and (**6**), rare cases of molecules having a four-membered $(MS)_2$ ring; (iv) the curious reaction leading to compounds (**5**) and (**6**); and (v) the *X*-ray data on compounds (**4**) (Figure 1) and (**5**) (Figure 2); see also Table 1.

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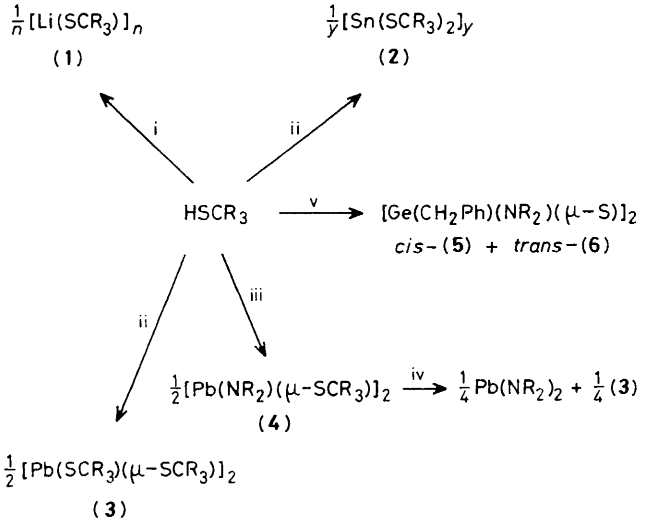
† Ölander numbering.

‡ No reprints available.

Table 1. Crystal data and refinement parameters for compounds (**4**) and (**5**).[a]

Compound	(**4**)	(**5**)
M	1262.46	696.46
Crystal system	Orthorhombic	Triclinic
a/Å	15.918(2)	9.075(1)
b/Å	9.250(4)	12.200(3)
c/Å	19.546(4)	17.834(9)
α/°	90	72.98(3)
β/°	90	84.41(2)
γ/°	90	82.72(1)
U/Å^3	2878.0	1868.9
Z	2	2
D_c/g cm^{-3}	1.46	1.24
$F(000)$	1264	728
Space group	$Pmn2_1$	$P\bar{1}$
X-rays, μ/cm^{-1} [b]	Mo-K_α/61.82	Cu-K_α/49.8
2θ limits/°	50	100
Reflections used in refinement $I > \sigma(I)$	1498	2457
R	0.083	0.082
R'	0.088	0.108

[a] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication. [b] $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\lambda(\text{Cu-}K_\alpha) = 1.5418$ Å.



Scheme 1. R = SiMe$_3$. *Reagents and conditions:* i, LiBu^n–C$_6$H$_{14}$, 20 °C; n-C$_6$H$_{14}$, 20 °C; ii, M′(NR$_2$)$_2$ (M′ = Sn or Pb), n-C$_{16}$H$_{14}$, 20 °C; iii, Pb(NR$_2$)$_2$, OEt$_2$, 20 °C [orange crystals of (**4**) from OEt$_2$]; iv, n-C$_6$H$_{14}$ or C$_6$D$_6$, 20 °C; v, PhMe, reflux [pale yellow crystals of (**5**) from n-C$_5$H$_{12}$ at −30 °C].

As for (ii), attempts to make compounds such as Sn(NR$_2$)(SAr) have led to the symmetrical redistribution products Sn(NR$_2$)$_2$ and Sn(SAr)$_2$. Doubtless the kinetic stability of compound (**4**) is due, at least in part, to its dimeric structure. The choice of solvent is critical: in a hydrocarbon, redistribution of (**4**) was observed.

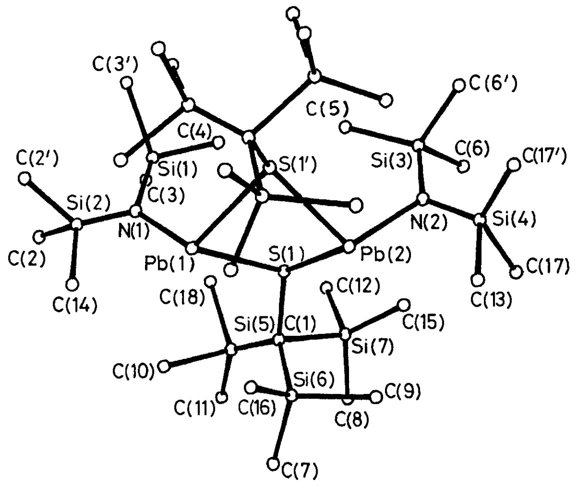


Figure 1. The molecular structure and atom numbering scheme for [Pb(NR$_2$)(μ-SCR$_3$)]$_2$ (R = SiMe$_3$), (**4**). Some dimensions are: Pb–S(1) 2.88(2), Pb(2)–S(1) 2.74(2), S(1)–C(1) 1.88(3), Pb(1)–N(1) 2.07(5), Pb(2)–N(2) 2.35(5), Si(1)–N(1) 1.89(6), Si(2)–N(1) 1.55(5) Å; S(1)–Pb(1)–S(1′) 76.3(4), S(1)–Pb(2)–S(1′) 81.2(4), Pb(1)–S(1)–Pb(2) 90.0(2)°. The geometry at N is *ca.* trigonal planar.

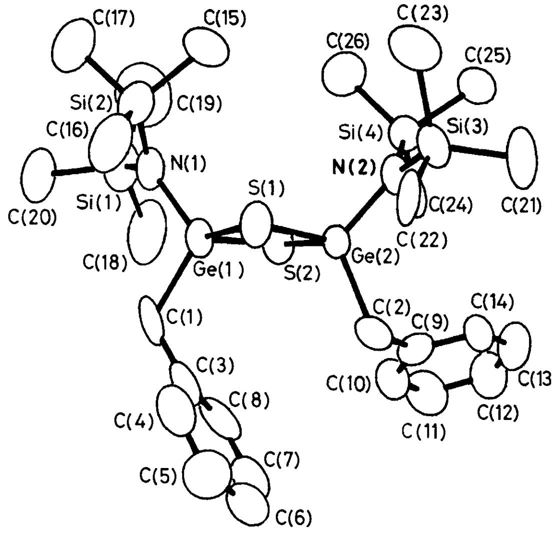


Figure 2. The molecular structure and atom numbering scheme for *cis*-[Ge(CH$_2$Ph)(NR$_2$)(μ-S)]$_2$ (R = SiMe$_3$), (**5**). Some dimensions are: Ge(1)–S(1) 2.230(5), Ge(1)–S(2) 2.248(6), Ge(2)–S(1) 2.254(6), Ge(2)–S(2) 2.241(5), <Ge–N> 1.82(2), <Ge–C> 1.96(2), <Si–N> 1.76(2) Å; <S–Ge–S> 95.5(3), <Ge–S–Ge> 84.2(2), Ge(1)–C(1)–C(3) 114(1), S(1)–Ge(1)–N(1) 114.5(5), S(1)–Ge(1)–C(1) 111.2(6)°. The geometry at N is *ca.* trigonal planar.

With regard to (iii), when first prepared [Ge(CH$_2$Ph)(NR$_2$)(μ-S)]$_2$ exists in C$_6$D$_6$ solution as a mixture of the *cis*- (**5**) and *trans*- (**6**) isomers, as shown by singlets in the ^{1}H n.m.r. spectra at δ 0.19 and 0.23 [Si(CH_3)$_3$] and at 2.52 and 3.06 (CH_2Ph), and in the ^{13}C n.m.r. spectra at δ 5.25 and 5.25 [Si(CH$_3$)$_3$] and at 40.69 and 42.79 (CH$_2$Ph).

With reference to (iv), the reaction pathway leading to compounds (**5**) and (**6**) [from Ge(NR$_2$)$_2$ and HSCR$_3$, in refluxing toluene] remains uncertain. However, free radical participation is probable. There was no reaction between Ge(NR$_2$)$_2$ and PhMe under the same conditions.

Concerning (v), the only X-ray data previously available on group 14 cyclodi(metalthiano) species related to [SiMe$_2$(μ-S)]$_2$[5] and [MBu$^t_2$(μ-S)]$_2$ (M = Ge[6] or Sn[7]).

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